

03068 VAT

WATER-DILUTABLE ALKYD RESINS, METHOD FOR THE PRODUCTION
AND THE UTILIZATION THEREOF

Field of the invention

- 5 The invention relates to water-dilutable alkyd resins.
It also relates to a process for the preparation thereof
and the use thereof, in particular for formulation of
high-gloss top coat paints.

Background of the Invention

- 10 In AT-B 400 719, a process is disclosed where water-
dilutable alkyd resins are prepared in a two-stage
process, a copolymer of vinyl monomers and a mass
fraction of from 25 to 50 % of unsaturated fatty acids
first being prepared. This copolymer is esterified with
15 further unsaturated fatty acids, polyols and low-molar-
mass dicarboxylic acids in a subsequent step to give an
alkyd resin which can be emulsified in water.

- The alkyd resins prepared in this way need to be improved
with respect to their gloss. There are likewise problems
20 when these alkyd resins are used for the formulation of
paints, areas that have already been coated drying too
rapidly which complicates adhesion of adjacent paint
layers.

- Providing a water-soluble alkyd resin which dries less
25 rapidly and shows a better gloss in the paint films
produced therefrom is therefore needed.

Summary of the Invention

- The invention relates to water-dilutable alkyd resins **ABC**
comprising units derived from unsaturated fatty acids **C**
30 which are bonded via ester groups to graft polymers of
vinyl monomers **B** on alkyd resins **A**. "Vinyl monomers" are
meant to encompass, in the context of this invention,

olefinically unsaturated monomers that can be copolymerised with styrene or methyl methacrylate in a polymerisation initiated by free radicals.

The invention also relates to a process for the
5 preparation of water-dilutable alkyd resins **ABC**, wherein an alkyd resin **A** is initially prepared in the first step by polycondensation of dicarboxylic acids **A1**, aliphatic monocarboxylic acids **A2** having from 2 to 40 carbon atoms, aliphatic linear, branched or cyclic alcohols **A3** having
10 at least two hydroxyl groups and optionally aliphatic mono- or diepoxides **A4**, which is then mixed in the second step with unsaturated fatty acids **B2**, and the mixture obtained in this way is reacted in the third step with vinyl monomers **B** selected from the group consisting of
15 vinyl monomers **B1** containing carboxyl groups, hydrophilic vinyl monomers **B4** and further vinyl monomers **B3** without hydroxyl or carboxyl groups, under conditions for free-radical polymerisation, graft polymers of the vinyl monomers **B1**, **B3** and **B4** with the alkyd resins **A** and the
20 fatty acids **B2** being formed, and these, with further unsaturated fatty acids **C**, are at least partly esterified with one another under condensation conditions and with splitting off of water, the fatty acids **C** preferably containing at least two olefinic double bonds per
25 molecule, and these being conjugated in a particularly preferred embodiment.

Finally, the invention relates to a method of use of the water-dilutable alkyd resins **ABC** according to the invention for the preparation of paints of improved
30 gloss.

Detailed Description of the Preferred Embodiments

The alkyd resins **A** contain units of dicarboxylic acids **A1**, aliphatic monocarboxylic acids **A2** having from 2 to 40 carbon atoms, aliphatic linear, branched or cyclic
35 alcohols **A3** having at least two hydroxyl groups, and

optionally aliphatic di- or monoepoxides **A4**. Their number-average molar mass M_n is preferably 1,000 g/mol to 5,000 g/mol, and the weight-average molar mass is from approximately 2,000 g/mol to approximately 12,000 g/mol.

- 5 Their acid number is preferably from 0 mg/g to 20 mg/g, particularly preferably from 1 mg/g to 10 mg/g, and their hydroxyl number is from 50 mg/g to 150 mg/g.

In this context, the dicarboxylic acids **A1** are chosen from saturated or unsaturated linear, branched and cyclic
 10 aliphatic dicarboxylic acids having from 2 to 40 carbon atoms and from aromatic dicarboxylic acids having from 8 to 20 carbon atoms, or from anhydrides thereof if these exist. Malonic acid, succinic acid, maleic acid, adipic acid, 1,2-, 1,3- and 1,4-cyclohexanedicarboxylic acid,
 15 dimerised fatty acids and mixtures thereof, phthalic acid, terephthalic acid, isophthalic acid and tetrahydrophthalic acid and the anhydrides of the acids mentioned, if these exist, are preferred.

Suitable aliphatic monocarboxylic acids **A2** are linear and
 20 branched aliphatic monocarboxylic acids, which optionally contain at least one double bond, such as acrylic acid, methacrylic acid and the higher unsaturated acids, such as myristic acid, palmitoleic acid, petroselic acid, petroselaidic acid, oleic acid, elaidic acid, linoleic
 25 acid, linolenic acid, alpha- and beta-eleostearic acid, gadoleic acid, arachidonic acid, erucic acid and clupanodonic acid, and saturated fatty acids, such as caproic acid, capric acid, 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid,
 30 arachidic acid, behenic acid and lignoceric acid, in each case individually or in a mixture, in particular in the naturally occurring mixtures, such as linseed oil fatty acid, tall oil fatty acid, juvandel fatty acid or the fatty acid mixtures obtained from the native fats and
 35 oils, for example by saponification and isomerisation, such as conjugandel fatty acid.

Suitable aliphatic alcohols **A3** are di- and polyfunctional aliphatic linear, branched and cyclic alcohols having from 2 to 20 carbon atoms, such as e.g. ethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,6-hexanediol, 5 neopentyl glycol, glycerol, trimethylolpropane, pentaerythritol, ditrimethylolpropane and dipentaerythritol. Formals of tri- or polyhydric alcohols, such as trimethylolpropane monoformal or pentaerythritol monoformal, are likewise suitable.

10 The aliphatic mono- or diepoxides **A4** optionally also used are preferably esters of glycidyl alcohol or ethers of glycidyl alcohol with monocarboxylic acids or monohydric alcohols having from 5 to 15 carbon atoms and esters of glycidyl alcohol with dicarboxylic acids or ethers with 15 diphenols or dialcohols, such as adipic acid, succinic acid, bisphenol A or bisphenol F or butanediol, hexanediol or cyclohexanedimethanol.

The vinyl monomers **B** are selected from the group consisting of vinyl monomers **B1** containing carboxyl 20 groups, unsaturated fatty acids **B2**, hydrophilic vinyl monomers **B4** having oligo- or polyalkylene glycol structures, C₂- and C₃-alkylene groups and mixtures thereof being preferred, and further vinyl monomers **B3** without hydroxyl or carboxyl groups.

25 Suitable vinyl monomers **B1** are olefinically unsaturated monocarboxylic acids, in particular acrylic and methacrylic acid. Suitable unsaturated fatty acids **B2** are those mentioned above under **A2**, and suitable vinyl monomers **B3** without functional groups apart from the 30 olefinically unsaturated group are, in particular, styrene, vinyltoluene, the alkyl esters of acrylic or methacrylic acid, such as methyl, ethyl, butyl or 2-ethylhexyl (meth)acrylate, vinyl acetate and the vinyl esters of versatic acid. Suitable monomers **B4** are, in 35 particular, ethers of olefinically unsaturated alcohols, such as especially that of allyl alcohol with monoalkoxy-

oligo- or -polyethylene glycol or monoalkoxy-oligo- or -polypropylene glycol or the monoalkoxy derivatives of mixed oligo- or polyglycols containing C₂- and C₃-alkylene units, as well as the half-esters of these monoalkoxy glycols with olefinically unsaturated carboxylic acids, such as acrylic and methacrylic acid. In this context, the degree of polymerisation of the oligo- or polyalkylene glycols is preferably from 2 to 20, the number of oxyethylene groups and the number of oxypropylene groups per molecule in each case preferably being from 0 to 10.

The unsaturated fatty acids **C** have from 6 to 40 carbon atoms and preferably at least two olefinic double bonds, which are preferably located so that at least two double bonds are conjugated with one another. Suitable fatty acids **C** are, in particular, the mixtures obtained from sunflower oil fatty acid or soya oil fatty acid by isomerisation, such as conjuvandol fatty acid, as well as the isomeric eleostearic acids.

The process according to the invention for the preparation of water-dilutable alkyd resins comprises, in the first step, the preparation of an alkyd resin **A** by polycondensation of dicarboxylic acids **A1**, aliphatic monocarboxylic acids **A2** having from 2 to 40 carbon atoms, aliphatic linear, branched or cyclic alcohols **A3** having at least two hydroxyl groups and optionally aliphatic di- or monoepoxides **A4**. In this context, the educts **A1** to **A3** are initially introduced into the reaction vessel and subjected to a condensation reaction, optionally with the addition of esterification catalysts based on organic compounds of transition metals or metals of main group four of the periodic table, the water of reaction being removed. If acids are employed in a stoichiometric excess here, the number of free carboxyl groups and therefore the acid number can be reduced by addition of aliphatic mono- or diepoxide compounds **A4**.

In the second step, the alkyd resins **A** prepared in this way are mixed with unsaturated fatty acids **B2**.

This mixture is then reacted in the third step with the further vinyl monomers chosen from vinyl monomers **B1**
5 containing carboxyl groups, hydrophilic vinyl monomers **B4** and further vinyl monomers **B3** without hydroxyl or carboxyl groups under free-radical polymerisation conditions, a grafted alkyd resin **AB** which contains carboxyl and hydroxyl groups being formed, as well as at
10 least partly grafted fatty acids **B2B**. Grafting is preferably carried out by a procedure in which the alkyd resin **A** and the fatty acids **B2** are dissolved in a solvent which is inert towards polymerisation and condensation reactions, namely aromatic or aliphatic hydrocarbons,
15 such as xylene or mixtures of aromatics, ether-like solvents, such as glycol mono- or diethers, or ketones, the vinyl monomers are metered in or mixed with the solutions and grafting is started by addition of free radical initiators, such as peroxides, peroxy acids or
20 azo compounds. According to the invention, it is preferable to add the free radical initiators in several portions.

In the third step, the graft copolymers **AB** are esterified with the at least partly grafted unsaturated fatty acids
25 **B2B** and optionally further fatty acids **C**, the esterification preferably being carried out with azeotropic distillation of the water of reaction. After at least partial neutralisation of the acid groups in the esterified graft copolymer **ABC**, this is dispersed in
30 water to a solids mass fraction of preferably 30 % to 60 %.

The graft polymer **ABC** formed preferably has a hydroxyl number of from 20 mg/g to 50 mg/g and an acid number of from 10 mg/g to 70 mg/g, preferably from 20 mg/g to
35 60 mg/g.

The aqueous dispersion obtained can be used in the formulation of alkyd resin paints which can be employed as clear paints, for example on wood, or as pigmented paints on substrates such as metals or plastics. The
 5 paints yield coatings of high gloss and low haze.

The examples which follow further explain the invention.

The acid number is defined according to DIN EN ISO 3682 as the quotient of that mass m_{KOH} of potassium hydroxide which is required to neutralise a sample to be analysed
 10 and the mass m_B of this sample (mass of the solid in the sample in the case of solutions or dispersions); its conventional unit is "mg/g". The hydroxyl number is defined according to DIN EN ISO 4629 as the quotient of that mass m_{KOH} of potassium hydroxide which contains
 15 exactly as many hydroxyl groups as a sample to be analysed and the mass m_B of this sample (mass of the solid in the sample in the case of solutions or dispersions); its conventional unit is "mg/g". The iodine number is defined according to DIN 53 241-1 as the quotient of that
 20 mass m_I of iodine which is added on to the olefinic double bonds, with decolouration, of a sample to be analysed and the mass m_B of this sample (mass of the solid in the sample in the case of solutions or dispersions); its conventional unit is "g/(100 g)" or "cg/g". The quantity
 25 previously referred to as "limiting viscosity number", called the "Staudinger index" J_g according to DIN 1342, Part 2.4, is the limiting value of the Staudinger function J_v at decreasing concentration and shear stress, where J_v is the relative change in viscosity based on the
 30 mass concentration $\beta_B = m_B/V$ of the dissolved substance B (with the mass m_B of the substance in the volume V of the solution), that is to say $J_v = (\eta_r - 1)/\beta_B$. In this formula, $\eta_r - 1$ denotes the relative change in viscosity, in accordance with $\eta_r - 1 = (\eta - \eta_s)/\eta_s$. The relative
 35 viscosity η_r is the quotient of the viscosity η of the solution analysed and the viscosity η_s of the pure solvent. (The physical meaning of the Staudinger index

is that of a specific hydrodynamic volume of the solvated polymer coil at infinite dilution and in the state of rest.) The unit conventionally used for J is "cm³/g"; formerly often "dl/g".

5 Examples

Example 1 (comparison)

1.1 Alkyd resin

240 g of soy bean oil fatty acid, 600 g of tall oil fatty acid having an iodine number of 150 cg/g, 285 g of
10 conjugandol fatty acid (having a mass fraction of approximately 50 % of conjugated fatty acids), 536 g of trimethylolpropane and 462 g of hexahydrophthalic anhydride were charged into a 3 l glass reactor equipped with a stirrer, thermometer, water separator and reflux
15 condenser and the mixture was homogenised. After the air had been displaced with nitrogen, the mixture was heated to 245 °C, with constant stirring. The mixture was kept at this temperature until its acid number had fallen to below 10 mg/g (approximately 6 hours). After cooling to
20 180 °C, 100 g of ®Cardura E 10 (glycidyl ester of versatic 10 acid, Resolution GmbH) were added in the course of thirty minutes and the reaction temperature was kept at 180 °C for a further hour. The acid number thereafter had fallen below 1 mg/g; the reaction was then
25 interrupted by cooling to room temperature. The resin (Staudinger index measured in chloroform: 6.2 cm³/g) was diluted to form a solution having a mass fraction of solids of 90 % by addition of glycol monobutyl ether.

1.2 Grafted alkyd resin

30 387.7 g of the alkyd resin from Example 1.1 were introduced into a glass reactor equipped with a stirrer, dropping funnel, thermometer and reflux condenser. The resin was heated to 140 °C under a flow of nitrogen, and a mixture of 50.9 g of butyl methacrylate, 99.4 g of

styrene, 47.7 g of methyl methacrylate, 43 g of methacrylic acid and 7.2 g of di-tert.-butyl peroxide was then metered in uniformly in the course of one hour. The mixture was subsequently reacted at this temperature for
5 four further hours. It was then cooled to 90 °C and a mixture of 20.8 g of a solution of ammonia in water (mass fraction of NH₃ approximately 25 %) and 114.6 g of desalinated water was added in the course of 30 minutes, under stirring. Thereafter, a further 730 g of water
10 were added over the course of approximately 90 minutes, during which the temperature dropped to approximately 40 °C.

Example 2

2.1 Alkyd resin A

15 240 g of soy bean oil fatty acid, 100 g of conjugandol fatty acid (having a mass fraction of approximately 50 % of conjugated fatty acids), 536 g of trimethylolpropane and 462 g of hexahydrophthalic anhydride were charged into a 2 l glass reactor equipped with a stirrer,
20 thermometer, water separator and reflux condenser and the mixture was homogenised. After the air had been displaced with nitrogen, the mixture was heated to 245 °C, with constant stirring. The mixture was kept at this temperature until its acid number had fallen to
25 below 10 mg/g (approximately 4 hours). After cooling to 180 °C, 100 g of ®Cardura E 10 (glycidyl ester of versatic 10 acid, Resolution GmbH) were added in the course of 30 minutes and the reaction temperature was kept at 180 °C for one further hour. The acid number
30 thereafter had fallen below 1 mg/g; the reaction was then interrupted by cooling to room temperature. The resin was diluted to form a solution having a mass fraction of solids of 90 % by addition of xylene.

2.2 Grafted and esterified alkyd resin **ABC**

229 g of the alkyd resin from Example 2.1 and 96 g of tall oil fatty acid having an iodine number of 150 cg/g were introduced into a glass reactor with a stirrer, dropping funnel, reflux condenser, water separator and thermometer; the resin was heated to 140 °C under a flow of nitrogen. A mixture of 50.9 g of n-butyl methacrylate, 99.4 g of styrene, 47.7 g of methyl methacrylate, 43 g of methacrylic acid and 7.2 g of di-tert.-butyl peroxide was metered in uniformly at this temperature in the course of six hours. The reaction was continued at this temperature for four further hours; thereafter 29.6 g of conjugandol fatty acid were added, the mixture was heated to 175 °C and the solvent xylene was distilled off under reduced pressure. Esterification was continued at the same temperature until a Staudinger index of 12 g/cm³ (measured in chloroform) was reached. 57.6 g of glycol monobutyl ether were subsequently added and the mixture was cooled to 90 °C. A mixture of 20.8 g of a solution of ammonia in water (mass fraction of NH₃ approximately 25 %) and 114.6 g of desalinated water was added in the course of 30 minutes, under stirring. Thereafter, a further 730 g of water were added over the course of approximately 90 minutes, during which the temperature dropped to approximately 40 °C.

Example 3

3.1 Alkyd resin **A**

240 g of soy bean oil fatty acid, 100 g of conjugandol fatty acid (having a mass fraction of approximately 50 % of conjugated fatty acids), 536 g of trimethylolpropane and 462 g of hexahydrophthalic anhydride were charged in a 2 l glass reactor equipped with a stirrer, thermometer, water separator and reflux condenser and the mixture was homogenised. After the air had been displaced with nitrogen, the mixture was heated to 245 °C, with constant stirring. The mixture was kept at this temperature until

its acid number had fallen to below 10 mg/g (approximately 4 hours) and the reaction was then interrupted by cooling to room temperature. The resin was diluted to form a solution having a mass fraction of solids of 90 % by addition of xylene.

3.2 Grafted and esterified alkyd resin **ABC**

229 g of the alkyd resin from Example 3.1 and 96 g of tall oil fatty acid having an iodine number of 150 cg/g were charged into a glass reactor equipped with a stirrer, dropping funnel, reflux condenser, water separator and thermometer; the resin was heated to 140 °C under a flow of nitrogen. A mixture of 50.9 g of n-butyl methacrylate, 99.4 g of styrene, 47.7 g of methyl methacrylate, 43 g of methacrylic acid and 7.2 g of di-tert.-butyl peroxide was metered in uniformly at this temperature in the course of six hours. The reaction was continued at this temperature for four further hours; thereafter 29.6 g of conjuvandol fatty acid were added, the mixture was heated to 175 °C and the solvent xylene was distilled off under reduced pressure. Esterification was continued at the same temperature until a Staudinger index of 12 g/cm³ (measured in chloroform) was reached. 57.6 g of glycol monobutyl ether were subsequently added and the mixture was cooled to 90 °C. A mixture of 20.8 g of a solution of ammonia in water (mass fraction of NH₃ approximately 25 %) and 114.6 g of desalinated water was added in the course of 30 minutes, under stirring. Thereafter, a further 730 g of water were added over the course of approximately 90 minutes, during which the temperature dropped to approximately 40 °C.

Examples 4 to 6

The alkyd resins **A** of Examples 4.1 to 6.1 were prepared in analogy to Example 3, the starting substances listed in the following table being employed.

Table 1 Alkyd resins **A** (composition of the reaction mixture)

Example		4.1	5.1	6.1
Soy bean oil fatty acid	g	240	240	260
Conjuvandol fatty acid	g		22	20
Trimethylolpropane	g	536	120	
Pentaerythritol	g			115
Hexahydrophthalic anhydride	g	462		
Isophthalic acid	g		117	
Phthalic anhydride	g			91
Benzoic acid	g		60	
Water separated by distillation	g	-66.4	-27.3	-28.6
Xylene	g	130.5	134.0	51.0
Acid number of the alkyd resin A	mg/g	6.7	14.1	3.1
Staudinger index of the alkyd resin A	cm ³ /g	5.3	6.2	6.1

- 5 The alkyd resins **A** prepared in this way (solutions having a mass fraction of solids of 90 g of the resin in 100 g of the solution) were then reacted with the monomers mentioned in Table 2 under conditions for a free-radical polymerisation. During this procedure, the alkyd
- 10 resins **A** were first mixed with an additional amount of a fatty acid **B2** and the mixture was heated to 140 °C under a nitrogen blanket. A mixture of the said monomers **B** with the initiator was then added dropwise over a period of 360 minutes. When the addition had ended, the
- 15 temperature was maintained for approximately 250 minutes more; thereafter the further fatty acids **C** were admixed, the mixture was heated to approximately 175 °C and the water of reaction was separated by azeotropic distillation. Esterification was continued until a
- 20 Staudinger index of the alkyd resin **ABC** of approximately 12 cm³/g was reached. The solvent xylene was then removed by distillation under reduced pressure and, after cooling, the product was adjusted to a solids mass fraction of approximately 38 % by addition of butyl
- 25 glycol, neutralising agent and two portions of water.

Table 2 Composition of the emulsions of the condensed and grafted alkyd resins

Example		4.2	5.2	6.2
Alkyd resin A of Example		4.1	5.1	6.1
Mass of the alkyd resin solution (90 %)	g	208.2	504.0	198.0
Linseed oil fatty acid	g		72	
Tall oil fatty acid	g	96		71
Polyethylene glycol monoallyl ether (®Maxemul 5010)	g			3.0
n-Butyl methacrylate	g	50.9	53.0	52.0
Styrene	g	99.4	11.0	20.0
Methyl methacrylate	g	47.7		
Methacrylic acid	g	43.0	36.0	25.0
®Bisomer PPA6S (methacrylic acid ester of polypropylene glycol)	g		3.0	
Di-tert.-butyl peroxide	g	7.2	5.0	7.0
Conjuvandol fatty acid	g	45.6		
Ricinene fatty acid	g		55	
Water separated by azeotropic distillation	g	-9.6	-9.1	-4.7
Xylene distillate	g	-20.8	-151.4	-19.8
Butyl glycol	g	57.6	85.0	40.0
Water	g	114.6	716.0	300.0
Aqueous ammonia solution (25 %)	g	20.8	23.0	17.0
Acid number of the alkyd resin ABC	mg/g	53	53	47
Staudinger index measured in chloroform	cm ³ /g	11.9	12.1	13.1
mass fraction of solids *	%	38.6	37.2	38.0
Dynamic viscosity of the solution	mPa·s	530	4,500	2,500
pH (10 % strength solution in water)		8.7	7.0	8.6
Mass fraction of polymer B in the alkyd resin ABC	%	42	18	27
Acid number, based on the mass of polymer B	mg/g	113	219	152
Mass fraction of the fatty acids in the alkyd resin ABC	%	34	30	54

*mass fraction of solids measured via the dry residue in
5 accordance with DIN 55 671.

Paints were prepared from the alkyd resin dispersions according to Examples 1 to 4 in accordance with the following recipes:

Table 3 Paint recipes

Water-dilutable alkyd resin of Example		1	2	3	4
Mass of the dispersion	g	68.2	67.4	68.2	68.4
Thickener (®Optiflo H 600) ^a	g	0.5	0.5	0.5	0.5
Siccative combination (Cobalt ®Aqua 7) ^b	g	0.2	0.2	0.2	0.2
Anti-skinning agent (butanone oxime)	g	0.3	0.3	0.3	0.3
Pigment paste ^c	g	29.4	29.4	29.4	29.4
Completely desalinated water	g	7	12	12	12
Dynamic viscosity (10^4 s^{-1} , 23 °C)	mPa·s	115	95	100	90
pH (DIN ISO 976)		8.8	8.8	8.8	8.8
Non-tacky after	min	30	30	30	60
Through-drying after 24 hours ^d		20	20	20	20
Gloss 20° (BYK Gardner)		18	86	87	89
Gloss 60° (in accordance with DIN 67 530)		61	92	94	96
Haze (BYK Gardner, ASTM E 430)		103	21	30	24

a Süd-Chemie AG, Moosburg

5 b Borchers GmbH, Monheim

c Pigment paste: composition see Table 4

d Through drying: determined by performing a scratch trial with the fingernail 24 hours after application of the paint to a glass plate; "10" means "no attack" = good; "50" means "film smeary, can easily be removed from the plate" = poor

o-o-o-o